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## EUROPEAN PATENT APPLICATION

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⑯ Process for producing propylene polymer.

⑰ A process for producing a propylene polymer having a carbonyl group at the terminal, said process comprising polymerizing propylene to give a living propylene polymer in the presence of a catalyst composed of beta-diketone vanadium chelate and an aluminum compound represented by the formula  $R_2A_1X$  (wherein R is a hydrocarbon group having 1 to 8 carbon atoms and X is a halogen atom), and reacting the living propylene polymer with a carbonylating agent.

EP UTILISATION

1        'PROCESS FOR PRODUCING PROPYLENE POLYMER'

2        The present invention relates to a process for producing a  
3        propylene polymer having a carbonyl group at the terminal.

4        Prior art

5        It is known that if carbon monoxide is during olefin polymeriza-  
6        tion in the presence of a Ziegler-Natta catalyst, the polymerization  
7        is suspended, with the result that carbon monoxide is interposed  
8        between the transition metal-polymer bond. In this case, various  
9        chain transfer reactions and termination reactions are operative so  
10      that the carbonylation at the terminal takes place in only the few  
11      polymer chains which are living at the moment of carbonylation. It  
12      is also a feature of polymerizations of this prior art type that they  
13      produce polymers with broad molecular weight distribution ( $M_w/M_n > 2$ ).

14      Problems to be solved by the invention

15      It is an object of the present invention to provide a nearly  
16      monodisperse propylene polymer in which every polymer chain has a  
17      carbonyl group.

18      The present inventors had previously found that a nearly mono-  
19      disperse living polypropylene is formed when propylene is polymerized  
20      using a catalyst composed of  $V(\text{acetylacetone})_3$  and  
21       $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ . [Makromol. Chem. 180, 1359 (1979); and  
22      Macromolecules., 12, 814 (1979)]

23      The present inventors found that when this living polypropylene  
24      is reacted with a carbonylating agent such as carbon monoxide,  
25      carbonyl groups can be introduced into the terminals of almost all  
26      the polymer chains. The present invention was completed based on  
27      this finding.

28      Means to solve the problems

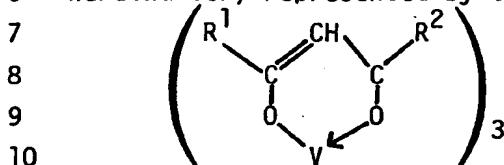
29      Summary of the invention

30      The gist of the invention resides in a process for producing a  
31      propylene polymer having a carbonyl group at the terminal, said  
32      process comprising polymerizing propylene to give a living propylene  
33      polymer in the presence of a catalyst composed of beta-diketone  
34      vanadium chelate and an aluminum compound represented by the formula  
35       $\text{R}_2\text{AlX}$  (where R is a hydrocarbon group having 1 to 8 carbon atoms

1 and X is a halogen atom), and reacting the living propylene polymer  
2 with a carbonylating agent.

3 Catalyst

4 The catalyst system used in this invention is composed of  
5 beta-diketone vanadium chelate (referred to as the vanadium compound  
6 hereinafter) represented by the formula below:



1 cyclopropane and cyclohexane), and aromatic hydrocarbons (such as  
2 benzene, toluene, and xylene).

3 The homopolymerization of propylene or the random copolymeriza-  
4 tion of propylene with comonomer should preferably be accomplished by  
5 adding in succession a solution of the aluminum compound and a solu-  
6 tion of the vanadium compound to a solution of propylene or a solu-  
7 tion of propylene and comonomer dissolved in a solvent.

8 In the homopolymerization of propylene or the random copolymeri-  
9 zation of propylene with comonomer, the polymerization catalyst is  
10 used in such an amount that the vanadium compound is  $1 \times 10^{-4}$  to  
11  $0.01 \text{ mol}$ , preferably  $5 \times 10^{-4}$  to  $5 \times 10^{-3} \text{ mol}$ , and the organo-  
12 aluminum compound is  $1 \times 10^{-3}$  to  $0.1 \text{ mol}$ , preferably  $5 \times 10^{-3}$  to  
13  $0.01 \text{ mol}$ , for 1 mol of propylene or 1 mol of propylene and comonomer  
14 in all. In addition, the amount of the organoaluminum compound  
15 should be 5 to 25 mol for 1 mol of the vanadium compound.

16 The molecular weight and yield of the living propylene homo-  
17 polymer or the living propylene random copolymer may be adjusted by  
18 changing the reaction temperature and reaction time. If the poly-  
19 merization temperature is low, particularly below  $-50^{\circ}\text{C}$ , the  
20 resulting polymer has a molecular weight distribution which is close  
21 to that of monodisperse polymer. Polymerization at  $-65^{\circ}\text{C}$  or below  
22 provides a living polymer having an  $\bar{M}_w/\bar{M}_n$  of 1.05 to 1.40 (where  $\bar{M}_w$   
23 is the weight-average molecular weight and  $\bar{M}_n$  is the number-average  
24 molecular weight).

25 The polymerization reaction permits the use of a reaction  
26 accelerator such as anisole, water, oxygen, alcohols (methanol,  
27 ethanol, isopropanol, etc.), and esters (ethyl benzoate, ethyl  
28 acetate, etc.). The reaction accelerator is used usually in an  
29 amount of 0.1 to 2 mol for 1 mol of the vanadium compound.

30 The comonomer in the living random copolymer composed of propy-  
31 lene and comonomer usually accounts for up to 80 wt%. This value can  
32 be adjusted by changing the amount of comonomer used at the time of  
33 living polymerization. When the amount of comonomer, especially  
34 ethylene, is increased, the resulting copolymer has a broad molecular  
35 weight distribution. This is undesirable. Where a living copolymer  
36 of high ethylene content with a narrow molecular weight distribution  
37 is to be produced, polymerization should preferably be performed in  
38 the following manner. That is, living polymerization for a very

1 small amount of propylene should be performed before living copoly-  
2 merization for propylene and ethylene. This permits the introduction  
3 of a large amount of ethylene into the copolymer, while keeping the  
4 molecular weight distribution of the living copolymer narrow. This  
5 polymerization method is illustrated with an example below. At  
6 first, propylene alone is supplied to the polymerization system to  
7 produce living polypropylene having a number-average molecular weight  
8 of preferably 500 to 2,000. Then, ethylene is supplied in the  
9 presence of a large amount of unreacted propylene monomer to continue  
10 living polymerization until the random copolymerization of ethylene  
11 and propylene comes to an end.

12 The thus obtained living homopolymer of propylene or living  
13 random copolymer of propylene and comonomer is made into a living  
14 block copolymer by living polymerization with a comonomer. This is  
15 accomplished by supplying a comonomer (which is different from the  
16 one used in the living random copolymerization with propylene) to the  
17 system in which the living homopolymer or living random copolymer and  
18 propylene are present, and performing living polymerization in the  
19 same manner as mentioned above. Usually, the comonomer accounts for  
20 up to 50 wt% in the block portion of the block copolymer. This  
21 amount can be adjusted by changing the amount of the comonomer used  
22 at the time of block copolymerization.

23 According to the above-mentioned method, it is possible to  
24 produce a living propylene polymer having a number-average molecular  
25 weight (in terms of propylene [to be repeated hereinafter]) of about  
26 500 to about 1,000,000 which is similar to monodisperse polymers.

#### 27 Carbonylating process

28 When the living propylene polymer comes into contact with a  
29 carbonylating agent, the living polymerization stops and, at the same  
30 time, the carbonylation proceeds so that a carbonyl group is intro-  
31 duced into the terminal of the polymer chain. Thus the carbonylation  
32 of the living propylene polymer is accomplished.

33 Examples of the carbonylating agent that can be used include  
34 carbon monoxide and carbon dioxide. They may be used as such or  
35 after dilution with an inert gas or liquid.

36 The reaction is performed at atmospheric pressure or under pres-  
37 sure, at a temperature of -100°C to +100°C, preferably -80°C to 0°C,  
38 for 5 minutes to 10 hours.

1       Incidentally, "carbonylation" as used herein means the intro-  
2       duction of the >C=O bond into the polymer molecule.

3       The propylene polymer which has undergone carbonylation is  
4       separated and recovered by the addition of alcohol (methanol,  
5       ethanol, etc.) to the reaction system.

6       In this way it is possible to produce a propylene polymer having  
7       an Mn of about 500 to about 1,000,000 which is similar to mono-  
8       disperse polymers, said propylene polymer being characterized by that  
9       the carbonyl group is introduced into the terminal of almost every  
10      polymer chain.

11      Effect of the invention

12      The process of this invention permits the efficient production of  
13      a propylene polymer in which the terminals of the polymer chains are  
14      carbonylated almost one-hundred percent selectively, the production  
15      involving no chain transfer reactions nor termination reactions. The  
16      polymer will find use as a compatibilizing agent, surface modifier,  
17      viscosity index improver, and drag reducer.

18      Examples

19      The invention is described in more detail with reference to the  
20      following examples. The following methods were used to characterize  
21      the resulting polymers.

22      Molecular weight and molecular weight distribution: Measured by  
23      the use of GPC (gel permeation chromatography), Model 150, made by  
24      Waters Co., Ltd. The solvent was trichlorobenzene. Measuring  
25      conditions: 135°C, solvent flow rate = 1.0 ml/min, and sample  
26      concentration = 0.15 wt/vol%. The column was GMH6 made by Toyo Soda  
27      Mfg. Co., Ltd. A calibration curve for polystyrene was made for the  
28      standard sample of monodisperse polystyrene available from Waters  
29      Co., Ltd. On the basis of this calibration curve, a calibration  
30      curve for the polypropylene was made according to the universal  
31      method.

32      Determination of carbonyl groups and methyl groups in propylene:  
33      Determined by the use of infrared spectrophotometer, Model A-3, made  
34      by Nippon Bunko Kogyo Co., Ltd., on the sample polymer formed into a  
35      75  $\mu$ m thick film.

36      Content of propylene in ethylene-propylene random copolymer:  
37      Determined by means of  $^{13}\text{C}$  NMR analysis. Model XL-200 with PFT  
38      (pulse Fourier transform unit), made by Varian Co., Ltd.

1 Conditions: 50 MHz, 120°C, pulse width 8.2  $\mu$ s  $\pi/3$ , pulse interval 4  
2 seconds, and integration 5000 times. The sample was dissolved in a  
3 2:1 mixed solvent of trichlorobenzene and heavy benzene.

4 Example 1

5 In a 200 ml autoclave, with atmosphere therein completely  
6 replaced with nitrogen gas, was placed toluene as a solvent, followed  
7 by cooling to -78°C. At this temperature, 35 g (0.83 mol) of  
8 propylene was added and dissolved in toluene. Then, 5 mmol of  
9  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  in toluene solution and 0.5 mmol of  $\text{V}(\text{acetyl}-$   
10  $\text{acetone})_3$  in toluene solution were added to start polymerization  
11 at -78°C. Thirty minutes later, carbon monoxide was fed into the  
12 autoclave under 30 atm, and the reaction was carried out for 1 hour  
13 with stirring. After completion of the reaction, carbon dioxide gas  
14 was purged, and the reaction solution was poured into ethanol which  
15 had been cooled to -78°C to precipitate the polymer. The resulting  
16 polymer was washed five times with 500 ml of ethanol and dried. The  
17 polymer (0.12 g) thus obtained was found to have a molecular weight  
18 and molecular weight distribution of  $\bar{M}_n = 2,800$  and  $\bar{M}_w/\bar{M}_n = 1.2$ ,  
19 respectively. It was a nearly monodisperse polymer.

20 Upon examination of the resulting polymer for infrared absorption  
21 spectrum, an absorption peak was observed at  $1,723 \text{ cm}^{-1}$  which is  
22 attributable to a carbonyl group. This indicates that carbonyl  
23 groups have been introduced into the polymer.

24 The number of carbonyl groups introduced into one molecule of the  
25 polymer chain was calculated from the following formula.

$$26 \quad [CO] = \left( \frac{41}{440} \right) \left( \frac{A1723}{A1460} \right) \left( \frac{\bar{M}_n}{42} \right)$$

28 where 41 and 440 denote the molar absorptivity at  $1,460 \text{ cm}^{-1}$  and  
29  $1,723 \text{ cm}^{-1}$  attributable to polypropylene and carbonyl group,  
30 respectively; A1723 and A1460 denote the absorption intensity at  
31  $1,723 \text{ cm}^{-1}$  and  $1460 \text{ cm}^{-1}$ , respectively;  $\bar{M}_n$  denotes the number-  
32 average molecular weight; and 42 denotes the molecular weight of  
33 propylene.

34 The calculated value of [CO] was 1.0, which apparently indicates  
35 that each molecule of the polymer has one molecule of carbonyl group.

1 Examples 2 to 5

2 The polymerization of propylene and the carbonylation reaction  
3 were performed in the same manner as in Example 1, except that the  
4 feed time and pressure of carbon monoxide were changed as shown in  
5 Table 1. The results are shown in Table 1.

6 Table 1

7	8	9	CO feed	CO pres	Polymer	Molecular	[CO] value	
			time (hour)	sure (atm)	yield (g)	$\bar{M}_n$		
10	1	1	0.5	30	0.12	2,800	1.2	1.0
11	2	2	1.0	1	0.48	5,800	1.2	0.9
12	3	3	1.0	30	0.44	5,900	1.2	1.2
13	4	4	2.0	30	0.94	11,500	1.2	1.3
14	5	5	20.0	30	9.42	120,000	1.3	1.2

15 Example 6

16 The polymerization of propylene and the carbonylation reaction were  
17 performed in the same manner as in Example 3, except that carbon  
18 monoxide was replaced by carbon dioxide at a pressure of 1 atm.  
19 There was obtained a polymer having a [CO] value of 0.8.

20 Example 7

21 In a 1 liter autoclave, with atmosphere therein completely  
22 replaced with nitrogen gas, was placed toluene as a solvent, followed  
23 by cooling to -78°C. At this temperature, 180 g (4.2 mol) of  
24 propylene was added and dissolved in toluene. Then, 0.1 mol of  
25  $Al(C_2H_5)_2Cl$  in toluene solution, 5 mmol of  $V(acetyl-$   
26 acetonate)<sub>3</sub> in toluene solution, and 2.5 mmol of anisole were added  
27 one after another to start the preliminary polymerization at -78°C.  
28 One hour later, nitrogen was purged and 4.6 g (0.16 mol) of ethylene  
29 was introduced. The copolymerization of ethylene and propylene was  
30 carried out at -78°C for 5 minute under a nitrogen atmosphere,  
31 whereby a living ethylene-propylene random copolymer was prepared.  
32 (Ethylene-propylene random copolymer is abbreviated as EPR herein-  
33 after.) Subsequently, carbon monoxide was fed at -78°C, and the  
34 reaction was carried out for 1 hour with stirring while keeping the  
35 pressure of carbon monoxide at 1 atm. Then 9.1 g of the desired  
36 polymer was obtained in the same manner as in Example 1. This

1 polymer was examined for molecular weight, molecular weight distri-  
2 bution, propylene content, and [CO] value. The results are shown in  
3 Table 2.

4 Examples 8 and 9

5 The synthesis of living EPR and the carbonylation reaction were  
6 performed in the same manner as in Example 7, except that the  
7 synthesis of living EPR was carried out under the different condi-  
8 tions. The results are shown in Table 2.

9 Table 2

10	11	Polymer 12 Example yield (g)	Mn	Molecular weight $\bar{M}_w/\bar{M}_n$	Propylene content (wt%)	[CO] value
13	7	9.1	27,200	1.2	50	0.8
14	8	14.3	43,000	1.3	50	1.2
15	9	1.03	7,500	1.2	75	1.1

16 Example 10

17 A living polypropylene was obtained in the same manner as in  
18 Example 7, except that the time for homopolymerization of propylene  
19 was changed to 10 hours. Ethylene was fed in the same manner as in  
20 Example 7 to carry out copolymerization, whereby a living block  
21 copolymer composed of polypropylene segments and EPR segments was  
22 synthesized. Subsequently, it was reacted with carbon monoxide in  
23 the same manner as in Example 7 to give 15.8 g of polymer having the  
24 following characteristic values.

25 Mn 50,000 ( $\bar{M}_n$  23,000 for polypropylene segments and  $\bar{M}_n$  27,000 for  
26 EPR segments)

27  $\bar{M}_w/\bar{M}_n$  1.20

28 [CO] value 1.3

CLAIMS:

1. An essentially monodisperse propylene polymer in which essentially every polymer chain is terminated with a carbonyl group.
2. The propylene polymer of claim 1 wherein the  $M_w/M_n$  is about 1 to 1.40.
3. The propylene polymer of claim 2 wherein the  $M_n$  is in the range of 500 to 1,000,000.
4. The propylene polymer of claim 1 which is homopoly-propylene.
5. The propylene polymer of claim 1 which is a random copolymer of propylene and ethylene or a alpha-olefin having 4 or more carbon atoms.
6. The propylene polymer of claim 1 which is a block polymer comprising homopolypropylene or co-polypropylene.
7. A process for producing essentially monodisperse propylene polymers being chain terminated with a carbonyl group, said process comprising polymerizing propylene to give a living propylene polymer in the presence of a catalyst system comprising a beta-diketone vanadium chelate and an aluminum alkyl halide represented by the formula  $R_2AlX$  wherein R is a hydrocarbyl group having 1 to 8 carbon atoms and X is halogen, and reacting the living propylene polymer with a carbonylating agent.
8. The process in accordance with claim 7 comprising homo-polymerizing propylene.
9. The process in accordance with claim 7 wherein propylene is copolymerized with ethylene or an alpha-olefin having 4 or more carbon atoms to yield living random copolymer.

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10. The process of claim 9 wherein the living random copolymer is further contacted with ethylene or an alpha-olefin having 3 or more carbon atoms to yield a living block polymer.

11. The process of claim 8 wherein living homopolypropylene is further contacted with ethylene or an alpha-olefin having 4 or more carbon atoms to yield a living block polymer.

12. The process of claim 7 wherein the vanadium chelate concentration to propylene or propylene comonomer concentration is in the range of  $1 \times 10^{-4}$  to 0.01 to about 1 mol and the aluminum alkyl to vanadium chelate mol ratio is in the range of about 5 - 25 to about 1.